Doctoral Thesis Abstruct

Development and application of spin dependent van der Waals density functional method

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Describing the van der Waals (vdW) force accurately is an important issue to research complex molecules, molecular crystals, molecules on surfaces, etc. Density functional theory (DFT) has a property of reasonable computational cost, compared with the calculation of quantum chemistry based on many-body wave functions. However the local density approximation (LDA) or generalized gradient approximation (GGA) does not include effect of the vdW force. One of promising methods, called vdW-DF, has been proposed by Dion et al. in 2004.

I have implemented this method into in-house DFT code, which employs a plane-wave basis set and ultrasoft pseudopotentials and applied it to some molecular crystals. It was found that the cell parameters obtained with vdW-DF show overall improvement compared with those obtained using the LDA/GGA.

Aside from improvement of vdW-DF itself, the extension to spin-polarized (magnetic) systems is important. I have proposed a practical way to extend the vdW-DF to spin-polarized system (vdW-DF-SGC) and applied the pair of oxygen molecules and solid oxygen (α- and δ-phases) in which there are both vdW and magnetic interactions among molecules. This extension enables us to study spin-polarized materials accurately without introducing empirical parameters in computational models. Using the new method, I have obtained an improved result in both the cohesive energy and equilibrium structure, compared with LDA/GGA results. I also found that the structural properties were determined by a delicate balance of magnetic and vdW interactions.

I. INTRODUCTION

Van der Waals (vdW) force has been well known for a log time and plays an important role for crystal and molecular structures of weakly-bonded materials. In order to analyze such kind of materials from first-principles, the nonlocal correction approach (vdW-DF) has been proposed[1]. However the method could not be applied to spin polarized system because it was based on the assumption of nonmagnetic system. There are some interesting systems, in which the vdW and magnetic interactions coexist; for example oxygen systems. Oxygen, which is one of abundant elements, has several unique characteristics. It is well known that the oxygen molecule has a spin-triplet ground state. Competition between magnetic and molecular interactions gave rich varieties of structural, electronic, and magnetic phases under the wide ranges of temperature and pressure, and high magnetic field[2–5].

In my doctoral research work, I implemented vdW-DF to in-house DFT code, developed the extension of vdW-DF to spin-polarized systems named vdW-DF-SGC (SGC means spin-polarization-dependent gradient correction), and investigated oxygen molecular systems and solid oxygens in addition to nonmagnetic molecular systems[6–8].

II. COMPUTATIONAL METHODS AND MODELS

I have implemented vdW-DF method into in-house DFT code. Apart from local correction energy function, this method has the nonlocal correlation functional, which takes into account a contribution from van der Waals interaction. This term can be written as follows;

$$E_{\mathrm{c}}^{\mathrm{nl}}[n] = \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}' n(\mathbf{r})\phi(q_0(\mathbf{r}), q_0(\mathbf{r}'), |\mathbf{r}-\mathbf{r}'|)\; n(\mathbf{r}'), \tag{1}$$

where the ϕ is function of $\mathbf{r}$ and $\mathbf{r}'$, $q_0(\mathbf{r})$ is function of density and its gradient on $\mathbf{r}$. Since the nonlocal correlation energy is formulated by double integral in real space, the computational cost is much larger than LDA/GGA. In order to overcome this problem, I took the order N log N method which was proposed by Wu and Gygi[9] who improved Román-Pérez and Soler's method[10].

In their method, the nonlocal correlation energy can be written as;

$$E_{\rm c}^{\rm nl}[n] \simeq \frac{1}{2}\sum_{\alpha\beta}\iint d\mathbf{r}d\mathbf{r}'\eta_\alpha(\mathbf{r})\phi(q_\alpha,q_\beta,|\mathbf{r}-\mathbf{r}'|)\eta_\beta(\mathbf{r}')$$
$$= \frac{\Omega}{2}\sum_{\alpha\beta}\sum_{\mathbf{G}}\eta_\alpha^*(\mathbf{G})\eta_\beta(\mathbf{G})\phi_{\alpha\beta}(|\mathbf{G}|), \tag{2}$$

where $\eta_\alpha(\mathbf{r}) = q_\alpha n(\mathbf{r})p_\alpha(\mathbf{r})/q_0(\mathbf{r})$. The q_α and q_β are just parameters to expand the kernel function ϕ and p_α is interpolation function. The $\eta_\alpha(\mathbf{G})$ and $\phi_{\alpha\beta}(|\mathbf{G}|)$ are Fourier coefficients of $\eta_\alpha(\mathbf{r})$ and $\phi(q_\alpha,q_\beta,|\mathbf{r}-\mathbf{r}'|)$. I used the cut-off q_α of 8 a.u. for the maximum value and the number of mesh is set to 31. I have confirmed a reliability of these parameters by realizing the previous results[1,7,9,10].

In the vdW-DF-SGC method which is extended to spin polarized systems, the exchange and correlation energy $E_{\rm xc}$ is written as

$$E_{\rm xc}[n_\uparrow,n_\downarrow] = E_{\rm x}^{\rm GGA}[n_\uparrow,n_\downarrow] + E_{\rm c}^{\rm LSDA}[n_\uparrow,n_\downarrow] + E_{\rm c}^{\rm nl}[n] + E_{\rm c}^{\rm GGA}[n_\uparrow,n_\downarrow] - E_{\rm c}^{\rm GGA}[n/2,n/2], \tag{3}$$

where $n_\uparrow$ and $n_\downarrow$ are the electron densities of spin-up and spin-down, respectively, and n is electron density ($n = n_\uparrow + n_\downarrow$). The last two terms in Eq. (3) represent a spin dependent gradient correction (SGC) which is given as follows:

$$E_{\rm c}^{\rm GGA}[n_\uparrow,n_\downarrow] - E_{\rm c}^{\rm GGA}[n/2,n/2] = \int d\mathbf{r}\; n(\mathbf{r})\left\{H(r_s,\zeta,t) - H(r_s,0,t)\right\}. \tag{4}$$

H, $r_{\rm s}$, ζ, and t are the gradient contribution, Seitz radius ($n = 3/4\pi r_s^3$), the relative spin-polarization, and the dimensionless density gradient proportional to $|\nabla n|$, respectively. I selected the functional form for H proposed by Perdew, Burke, and Ernzerhof (PBE)[11]. Because the nonlocal correlation energy of vdW-DF[1] had no contribution from SGC, as shown in Eq. (4), I took into account a contribution by using the PBE(GGA) correlation functional. Since $E_{\rm c}^{\rm nl}$ in Eq (3) contains all contributions of correlation energy except for local correlation energy in nonmagnetic case[1], to avoid a double counting problem, I used an energy difference between magnetic and nonmagnetic terms as a contribution from SGC.

The computational model α-O_2 has an antiferromagnetic ground state with the crystal structure of the $C2/m$ space group, as shown in Fig. 1. I used $8\times8\times8$ k-point set and large energy cutoffs for the plane wave basis (160 Ry and 960 Ry) to achieve the convergence in the pressure tensor, since the potential energy surface is very sluggish.

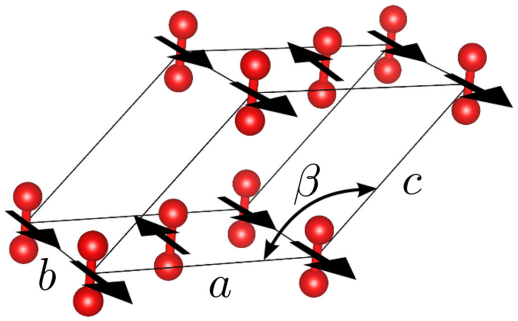

FIG. 1: Crystal structure of the solid oxygen in α phase. The arrows on molecules represent the magnetic moment.

III. RESULTS AND DISCUSSIONS

As shown in Table I, I report the structural parameters using LDA, GGA, vdW-DF, and vdW-DF-SGC. LDA severely underestimates the equilibrium volume by 43%, while PBE overestimates it, but the error is marginal (11%). However, this unexpectedly small error is caused by the error cancellation of the errors of a (-15%) and b (15 %). The error in c is also surprisingly small, but layer distance is overestimated by the underestimation of β, owing to lacking of van der Waals force. The underestimation of β is probably caused by an inaccurate description on the interlayer molecular interaction. On the other hand, the vdW-DF and vdW-DF-SGC also underestimate a and c, whereas b is overestimated, and as a result, the equilibrium volumes are consistently underestimated. Comparing to LDA/GGA results, that error is not so large and dramatically improved (e.g.: 5% on vdW-DF, 3% on vdW-DF-SGC). By taking into account the SGC effect, the lattice constant a is improved, indicating that our approach is good extension. I calculated the magnetic energy, defined by the energy difference between the ferromagnetic (F) and the antiferromagnetic(AF) states at the same AF crystal structure ($\Delta E_{\rm mag} = E^{\rm F} - E^{\rm AF}$). It is found that SGC term affects the antiferromagnetic interaction and destabilizes it. By emphasizing the SGC effect, the description of antiferromagnetic interaction may be improved. According to this idea, the improvement of vdW-DF-SGC approach have been done. It was found that attempt can describe more accurate antiferromagnetic interactions[12]. The energy $\Delta E_{\rm mag}$ and ΔE_b have same energy order, indicating that the vdW energy comparable to the magnetic one.

TABLE I: Optimized lattice parameters (a, b, c, and β), layer distance ($c_z = c\sin\beta$), equilibrium volume (V_0), binding energy of molecule (ΔE_b), magnetic energy ($\Delta E_{\rm mag}$). The value of $\Delta E_{\rm mag}$ on LDA could not be obtained owing to strong instability of ferromagnetic phase because LDA gave shrinked structure increasing stability of antiferromagnetic state. Experimental values are shown for comparison.

Functional	a (Å)	b (Å)	c (Å)	β (deg)	c_z (Å)	V_0 (Å^3)	ΔE_b (meV)	$\Delta E_{\rm mag}$ (meV)
LDA	3.29	3.28	4.05	113.9	3.70	19.93	552	–
GGA(PBE)	4.59	3.93	5.05	122.1	4.28	38.54	41	95
vdW-DF	4.68	3.68	4.70	125.2	3.84	33.05	221	118
vdW-DF-SGC	4.94	3.57	4.91	128.4	3.85	33.85	213	87
Expt.[13]	5.403	3.429	5.086	132.3	3.76	34.85		

IV. CONCLUSION

I have implemented vdW-DF method into in-house DFT code and proposed the extension to spin-polarized system (vdW-DF-SGC). I found that the vdW-DF-SGC method improves the description of the crystal structure on solid oxygen (α-phase). I also found that the structural properties were determined by a delicate balance of magnetic and vdW interactions. Although the results of other systems (nonmagnetic molecular crystals, other phases of solid oxygen, an absorption on ferromagnetic surface) are not shown here, vdW-DF and spin polarized vdW-DF approach have given accurate descriptions for molecular and crystal structures, compared with those obtained using local density and generalized gradient approximations.

Even though the present spin polarized version of vdW-DF must be improved further, the new scheme developed in the doctoral course will open a promising way to the study on magnetic vdW complex systems without models parameterized for particular systems, such as materials for organic spintronics, magnetic molecules surface systems, magnetic-cluster-containing molecular systems etc.

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学位論文審査報告書（甲）

１．学位論文題目（外国語の場合は和訳を付けること。）

Development and application of spin dependent van der Waals density functional method　（邦訳：スピン依存ファン・デル・ワールス密度汎関数法の開発・応用）

２．論文提出者　(1) 所　　属　数物科学　　専攻

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３．審査結果の要旨（600～650字）

小幡正雄氏の論文について，各審査委員が個別に検討し，面接調査および予備審査会の後，詳細に検討した。その後平成２８年７月２８日に開催された口頭発表の後に，審査委員会を開催し，協議の結果以下のように判定した。

小幡氏は，経験的パラメーターを導入せず（非経験的に）分散力（ファン・デル・ワールス力）を評価する計算手法の開発研究に取り組み，自ら考案した新手法，スピン依存ファン・デル・ワールス密度汎関数（vdW-DF）法を開発し，その有効性を実証した。この分散力は，電子密度の量子的揺らぎに起因するものであるが，無極性分子間に顕著に観測される力として知られる。分子間距離の６乗に反比例する引力とするモデル化が役立ってきたが，常に経験的パラメーターが導入され適用範囲に限界があった。2004年に分散力が電子密度の汎関数で定式化されて以来，世界的に開発・応用研究が精力的に行われてきた。小幡氏は，磁性物質群へ適用できる汎関数を世界で初めて具体的に構築した。この手法をvdW力により凝集した磁性物質である固体酸素等に適用し，分子間の磁気的相互作用とvdW相互作用を同時にかつ定量的に議論し，密度汎関数法に新たな予測力を導入することに成功した。研究成果は，vdW-DF法の適用範囲を格段に広げ，計算物質科学分野をはじめ多くの研究分野の進展に寄与するものと期待される。

以上のような成果をまとめた本論文は，博士（理学）の学位に値するものと判定した。

４．審査結果　(1) 判　　定（いずれかに○印）（合　格）・　不合格

(2) 授与学位　博　士（　理学　）